17. Domiano, P.; Nardelli, M.; Balsamo, A.; Macchia, B.; Macchia, F.; Meinardi, G. *J. Chem. Soc. Perkin Trans.* 2 **1978**, 1082.
18. Spry, D. O.; Bhala, A. R.; Spitzer, W. A.; Jones, N. D.; Swartzendruber, J. K. *Tetrahedron Lett.* **1984**, *25*, 2531.
19. Fernández, B.; Carballeira, L.; Ríos, M. A. *Biopolymers* **1992**, *32*, 97.
20. Marstokk, K. M.; M llendal, H.; Samdal, S.; Uggerud, E. *Acta Chem. Scand.* **1989**, *43*, 351.
21. Frau, J.; Coll, M.; Donoso, J.; Munoz, F.; Garcia Blanco, F. *J. Molec. Struc. (Theochem)* **1991**, *231*, 109.
22. Frau, J.; Donoso, J.; Munoz, F.; García Blanco, F. *J. Molec. Struc. (Theochem)* **1991**, *251*, 205.
23. Chung, S. K.; Chodosh, D. F. *Bull. Korean Chem. Soc.* **1989**, *10*, 185.

Generalization of Keesom Transformation in Multipole-Multipole Interaction Potentials

Chun-Woo Lee

Department of Chemistry, Ajou University, 5 Wonchun Dong, Suwon 441-749, Korea

Received June 29, 1995

In order to ease the treatment of anisotropic potential when developing the variational RRKM theory, we applied Fano-Racah's recoupling theory to the multipole-multipole interaction, resulting in the great simplification of the anisotropic potentials. The treatment appears as a generalization of Keesom transformation in case of dipole-dipole interaction and provides us with great insights to the characteristics of tensorial interactions in the multipole-multipole interaction system.

Introduction

Recently, there have been considerable interests[1] in fast, neutral gas phase reactions with no potential barriers along the reaction coordinates. The interest derives from their important role in areas such as atmospheric, combustion and interstellar chemistry. Another source of interest is the progress in the experimental methods for detecting small concentrations of very reactive molecules such as free radicals.

The reaction rate constants for these reactions have often been found to decrease with increasing temperature.[1] Recent Rice Ramsperger Kassel Marcus (RRKM) variational calculations[2,3,4] have produced the same trends and several qualitative explanations are available now. We also succeeded in solving the variational RRKM equations analytically under some reasonable constraints and under the long-range potential of type $V(R, \Omega)=R^{-s}A(\Omega)$.[5] Here Ω stands for the angular variables and $A(\Omega)$ is the anisotropic part of the potential. For the fast neutral gas phase reactions with no potential barriers, it is believed that long range potentials play an important role.[6] Long-range potentials result from multipole-multipole interactions. They are tensor forces and have a complicated angular denpendence. Simple long-range-potentials that ignore the complicated angular dependence have thus enjoyed the frequent employ.

Long ago, Keesom[7] found an interesting transformation that greatly simplifies the angular part of the dipole-dipole interactions. Let us consider two dipoles A and B. Let (θ_1, ϕ_1) and (θ_2, ϕ_2) be their spherical polar coordinates. The z axis is directed toward each other. Then the angular dependence is given by $2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1-\phi_2)$. By considering the transformation, $2\cos\theta_1 = g\cos\psi$, $\sin\theta_1 = \theta_1 = g\sin\psi$, Keesom showed that the angular dependenceis simplified as $g\cos\theta$. Thus Keesom transformation may be used to deal with the anisotropic nature of the dipole-dipole interaction.

On the other hand, Fano and Racah[8] discussed the tensorial nature of the dipole-dipole interaction in Appendix J of their book. The final formula surprisingly resembles Keesom transformation. We find that the final formula is actually equivalent to Keesom transformation. As Fano-Racah's approach can be easily generalized while Keesom transformation is not, we applied Fano-Racah's recoupling theory to the generalization of Keesom transformation. The result is surprisingly simple and takes the equivalent form of the simplest case of Keesom transformation. Our approach provides the insight to the nature of the anisotropic aspect of the multipole-multipole interactions which was not transparent in the past.

Keesom transformation and recoupling theory

Let us first summarize Fano-Racah's treatment of dipole-dipole interaction. The dipole-dipole interaction can be written as (see Appendix B. On the multipole expansion[9])

$$V=-(\vec{\mu}_1\cdot\nabla_1)(\vec{\mu}_2\cdot\nabla_2)\frac{1}{r}=(\vec{\mu}\cdot\nabla)(\vec{\mu}_2\cdot\nabla)\frac{1}{r}. \qquad (1)$$

The last equality follows from $-\nabla_2=\nabla_1=\nabla$ that derives from $\vec{r}=\vec{r}_1-\vec{r}^2$. Now we can utilize the recoupling theory to recouple $(\vec{\mu}_1\cdot\nabla)$ and $(\vec{\mu}_2\cdot\nabla)$. We couple ∇ and ∇ together and $\vec{\mu}_1$ $\vec{\mu}_2$ together:

$$(\vec{\mu}_1\cdot\nabla)(\vec{\mu}_2\cdot\nabla)=[[\mu_1{}^{[1]}\nabla^{[1]}]^{(0)}[\mu_2{}^{[1]}\nabla^{[1]}]^{(0)}]^{(0)}$$
$$=\sum_k[[\mu_1{}^{[1]}\mu_2{}^{[1]}]^{(k)}[\nabla^{[1]}\nabla^{[1]}]^{(k)}]^{(0)}\times((11)0(11)0|(11)k(11)k). \quad (2)$$

Now the recoupling constant can be related to 9-j symbol[9]

$$(j_{12}j_{34}|j_{13}j_{24})=[(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)]^{1/2}\begin{Bmatrix} j_1 & j_2 & j_{12}\\ j_3 & j_4 & j_{34}\\ j_{13} & j_{24} & j\end{Bmatrix}. \quad (3)$$

The recoupling constant $((11)0(11)0|(11)k(11)k)$ is obtained as $\sqrt{2k+1}/3$. We thus obtain the following relation

$$V=(\vec{\mu}_1\cdot\nabla)(\vec{\mu}_2\cdot\nabla)\frac{1}{r}$$
$$=3\sum_k\frac{\sqrt{2k+1}}{3}[[\mu_1{}^{[1]}\mu_2{}^{[1]}]^{(k)}[\nabla^{[1]}\nabla^{[1]}]^{(k)}]^{(0)}\frac{1}{r}$$
$$=\sum_k[[\mu_1{}^{[1]}\mu_2{}^{[1]}]^{(k)}\cdot[\nabla^{[1]}\nabla^{[1]}]^{(k)}]^{(k)}\frac{1}{r} \quad (4)$$

$[\nabla^{[1]}\nabla^{[1]}]^{(0)}$ is equivalent to Laplacian and $1/r$ is the solution of the Laplacian equation. Thus $k=0$ term vanishes. $[\nabla^{[1]}\nabla^{[1]}]^{(1)}$ term also vanishes as is well known in vector algebra. The reamining term can be simplified as follows

$$[\nabla^{[1]}\nabla^{[1]}]^{(2)}\frac{1}{r}=-[\nabla\times(\vec{r}/r^3)]^{(2)}=-(1/r^3)[\nabla\times\vec{r}]^{(2)}$$
$$-[\nabla(1/r^3)\times\vec{r}]^{(2)}. \quad (5)$$

The first term becomes zero because the differential operator lowers the rank by one and thus the rank of $\nabla\times\vec{r}$ becomes zero and has no second rank tensor elements. The second term is simplified as

$$[\nabla^{[1]}\nabla^{[1]}]^{(2)}\frac{1}{r}=(3/r^5)[\vec{r}\times\vec{r}]^{(2)}=(3/r^3)[\vec{u}\times\vec{u}]^{(2)}. \quad (6)$$

The set of contrastandard components of $\vec{u}$ coincides with the set of harmonic functions $C^{[1]}(\theta\phi)$. The tensor $[\vec{u}\times\vec{u}]^{(2)}$ has the set of contrastandard components $[C^{[1]}\times C^{[1]}]^{[2]}$. From Eq. (J.10) of Ref. 8,

$$[C^{[l_1]}\times C^{[l_2]}]^{[l]}=i^{l_1+l_2-l}(l_10l_20|l0)C^{[l]}. \quad (7)$$

The electrostatic energy becomes

$$V=\frac{\sqrt{6}}{r^3}[\mu_1{}^{[1]}\mu_2{}^{[1]}]^{[2]}\cdot C^{[2]}$$
$$=\frac{\sqrt{10}}{r^3}[\mu_1{}^{[1]}C^{[2]}]^{[1]}\cdot\mu_2{}^{[1]} \quad (8)$$

The last equation resembles Keesom transformation. We will show the equivalence between Eq. (8) and Keesom transformation.

Eq. (8) reveals that the equivalence may be obtained if $[\mu_1{}^{[1]}C^{[2]}]^{[1]}$ has polar coordinates $(\psi,\ \phi_2)$ and if we can find the relation between its polar coordinates and those of $\vec{\mu}_1$. Then θ is the angle between it and $\vec{\mu}_2$, as seen evidently from Eq. (8). The relation between their polar coordinates can be obtained by realizing the fact that ψ is the angle that $[\mu_1{}^{[1]}C^{[2]}]^{[1]}$ makes with the vector that connects the two dipoles. The latter is just $\vec{r}$ (see Appendix B). The set of contrastandard coordinates of $\vec{r}$ is just $C^{[1]}$. Therefore, let us consider the irreducible set of rank 0, $[[\mu_1{}^{[1]}C^{[2]}]^{[1]}C^{[1]}]^{[0]}$.

$$[[\mu_1{}^{[1]}C^{[2]}]^{[1]}C^{[1]}]^{[0]}$$
$$=[\mu_1{}^{[1]}[C^{[2]}C^{[1]}]^{[1]}]^{[0]}(((12)11)0|(1(21)1)0)$$
$$=[\mu_1{}^{[1]}[C^{[2]}C^{[1]}]^{[1]}]^{[0]}$$
$$=(2010|10)[\mu_1{}^{[1]}C^{[1]}]^{[0]}. \quad (9)$$

In the familar scalar product notation, Eq. (9) becomes

$$[\mu_1{}^{[1]}C^{[2]}]^{[1]}\cdot\vec{u}=\sqrt{3}\begin{pmatrix}2&1&1\\0&0&0\end{pmatrix}\vec{\mu}_1\cdot\vec{u}. \quad (10)$$

According to Keesom transformation, g may be considered to be defined so that the dipole-dipole interaction energy is given by $g\cos\theta/r^3$. Then as the dipole-dipole interaction energy is given by Eq. (8), the magnitude of $[\mu_1{}^{[1]}C^{[2]}]^{[1]}$ is given by $g\mu_1/\sqrt{10}$. Eq. (10) may, accordingly, be written as

$$\frac{1}{\sqrt{10}}\,g\cos\psi=\sqrt{3}\begin{pmatrix}2&1&1\\0&0&0\end{pmatrix}\cos\theta_1=\sqrt{\frac{2}{5}}\cos\theta_1. \quad (11)$$

We thus get $g\cos\psi=2\cos\theta_1$. In order to find the relation between $g\sin\psi$ and $\sin\theta_1$, let us consider the recoupling that yields the rank 1.

$$[[\mu_1{}^{[1]}C^{[2]}]^{[1]}C^{[1]}]^{[1]}$$
$$=\sum_k[\mu_1{}^{[1]}[C^{[2][1]}C^{[k]}]^{[1]}]^{[1]}((12)11)|1(21)k)^{[1]}$$
$$=\sum_k[\mu_1{}^{[1]}C^{[k]}]^{[1]}(2010|k0)((12)11|1(21)k)^{[1]}$$
$$=[\mu_1{}^{[1]}C^{[1]}]^{[1]}(2010|10)((12)11|1(21)1)^{[1]}. \quad (12)$$

The last equality follows from the parity restriction imposed on 3j symbol. The recoupling constant $((12)11|1(21)k)^{[1]}$ can be calculated by using the relation to the 6j symbol

$$(j_{12}j_3|j\,j_{23})^{[j]}=(-1)^{j_1+j_2+j_3+j}\sqrt{(2j_{12}+1)(2j_{23}+1)}\begin{Bmatrix} j_1 & j_2 & j_{12}\\ j_3 & j & j_{23}\end{Bmatrix}. \quad (13)$$

Then Eq. (12) becomes $(\mu_1\sqrt{10})[\mu_1{}^{[1]}C^{[1]}]^{[1]}$. The contrastandard set of rank 1 is related to the vector product as follows

$$[\mu_1{}^{[1]}C^{[1]}]^{[1]}=-\frac{1}{\sqrt{8}}\vec{\mu}_1\times\vec{u} \quad (14)$$

Likewise,

$$[[\mu_1{}^{[1]}C^{[2]}]^{[1]}C^{[1]}]^{[1]}=-\frac{1}{\sqrt{80}}\,g\mu_1\sin\psi. \quad (15)$$

From Eqs. (12), (14), and (15), we get $g\sin\psi=\sin\theta_1$.

Generalization of Keesom transformation

Let us first apply Fano-Racah's recoupling theory to the dipole-quadrupole interaction. As shown in Appendix B, the dipole-quadrupole interaction is given as

$$V_{1-2}=(\vec{\mu}_1\cdot\nabla)Q_2{}^{[2]}\cdot[\nabla^{[1]}\nabla^{[1]}]^{(2)}\frac{1}{r}$$
$$=\sum_k[[\mu^{[1]}1Q_2{}^{[2]}]^{[k]}[\nabla^{[1]}[\nabla^{[1]}\nabla^{[1]}]^{[2]}]^{[k]}]^{[0]}$$
$$((11)0(22)0|(12)k(12)k)^{[0]}. \quad (16)$$

The recoupling constant is obtained as

$$((11)0(22)0|(12)k(12)k)^{[0]}=(2k+1)\begin{Bmatrix}1&1&0\\2&2&0\\k&k&0\end{Bmatrix}=\sqrt{\frac{2k+1}{15}}. \quad (17)$$

Eq. (16) becomes

$$V_{1-2}=\frac{1}{\sqrt{15}}\sum_k[\mu_1^{[1]}Q_2^{[2]}]^{[k]}\cdot[[\nabla^{[1]}\nabla^{[1]}]^{(2)}\nabla^{[1]}]^{[k]}. \quad (18)$$

Let us first manipulate the second term of the right hand side of the last equation.

$$\left[[\nabla^{[1]}\nabla^{[1]}]^{(2)}\nabla^{[1]}\left(\frac{1}{r}\right)\right]^{[k]}=-\left[[\nabla^{[1]}\nabla^{[1]}]^{(2)}\left(\frac{\vec{r}}{r^3}\right)\right]^{[k]}$$
$$=\sum\left[\nabla^{[1]}\left[\nabla^{[1]}\frac{\vec{r}}{r^3}\right]^{[i]}\right]^{[k]}((11)21|1(11)i)^{[k]}$$
$$=\sum\left[\nabla^{[1]}\left[\nabla^{[1]}\frac{\vec{r}}{r^3}\right]^{[i]}\right]^{[k]}(-1)^{k+1}\sqrt{5(2i+1)}\begin{Bmatrix}1&1&2\\1&k&i\end{Bmatrix}. \quad (19)$$

$$\left[\nabla^{[1]}\left(\frac{\vec{r}}{r^3}\right)\right]^{[i]}=\frac{1}{r^3}[\nabla^{[1]}r^{[1]}]^{[i]}+\left[\nabla^{[1]}\left(\frac{1}{r^3}\right)r^{[1]}\right]^{[i]}$$
$$=\frac{1}{r^3}\delta_{i0}\sqrt{3}+\frac{3}{r^3}[\vec{u}\times\vec{u}]^{[i]}$$
$$=\frac{1}{r^3}\delta_{i0}\sqrt{3}+\frac{3}{r^3}C^{[i]}(1010|i0)$$
$$=\frac{3}{r^3}C^{[2]}(1010|20). \quad (20)$$

Let us define solid harmonic functions $C^{[k]}(\vec{r})\equiv r^kC^{[k]}(\theta\phi)$. In Appendix C, we derived the following relation

$$[\nabla^{[1]}C^{[k]}(\vec{r})]^{[k-1]}=\sqrt{k(2k+1)}C^{[k-1]}(\vec{r}). \quad (21)$$

By using Eq. (21), we obtain

$$\left[\nabla\left(\frac{1}{r^5}\right)C^{[2]}(\vec{r})\right]^{[k]}=-\frac{5}{r^4}(1020|30)C^{[3]}\delta_{k,3}. \quad (22)$$

Then

$$\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\frac{\vec{r}}{r^3}\right]^{[k]}=-\frac{1}{r^4}3\sqrt{\frac{2}{3}}5^2\begin{Bmatrix}1&1&2\\1&3&2\end{Bmatrix}(1020|30)C^{[3]}\delta_{k,3}, \quad (23)$$

and

$$\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\nabla^{[1]}\frac{1}{r}\right]^{[k]}=-\frac{1}{r^4}3\sqrt{\frac{2}{3}}5^2\begin{Bmatrix}1&1&2\\1&3&2\end{Bmatrix}(1020|30)C^{[3]}\delta_{k,3}. \quad (24)$$

As a whole, the dipole-quadrupole interaction becomes

$$V_{1-2}=(\vec{\mu}_1\cdot\nabla)Q_2^{[2]}\cdot[\nabla^{[1]}\nabla^{[1]}]^{(2)}\frac{1}{r}$$
$$=\frac{1}{\sqrt{15}}[Q_2^{[2]}\mu^{[1]}]^{[3]}\cdot C^{[3]}\times\left\{-\frac{1}{r^4}3\sqrt{\frac{2}{3}}5^2\begin{Bmatrix}1&1&2\\1&3&2\end{Bmatrix}(1020|30)C^{[3]}\right\}$$
$$=-\frac{\sqrt{6}}{r^4}[Q_2^{[2]}\mu^{[1]}]^{[3]}\cdot C^{[3]}. \quad (25)$$

Finally, we may transform the equation into a form of scalar product of the multipole moment with the field at that position generated by another multipole.

$$V_{1-2}=-\frac{\sqrt{6}}{r^4}[Q_2^{[2]}C^{[3]}]^{[1]}\cdot\mu^{[1]}\sqrt{\frac{3}{7}}((21)33|(23)11)^{[0]}$$
$$=-\frac{\sqrt{6}}{r^4}\sqrt{\frac{3}{7}}[Q_2^{[2]}C^{[3]}]^{[1]}\cdot\mu^{[1]}. \quad (26)$$

Therefore, the anisotropic part of dipole-quadrupole interaction is also as simple as dipole-dipole interaction as Keesom transformation shows.

Now let us apply the same technique to quadrupole-quadrupole interaction and see whether there is still only one kind of anisotropic interaction. As before, we will get the following term after some recoupling:

$$[[\nabla^{[1]}\nabla^{[1]}]^{[2]}[\nabla^{[1]}\nabla^{[1]}]^{[2]}]^{[k]}\frac{1}{r}$$
$$=-\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\left[\nabla^{[1]}\frac{C^{[1]}(\vec{r})}{r^3}\right]^{[2]}\right]^{[k]}$$
$$=-\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\left[\frac{-3}{r^5}C^{[1]}(\vec{r})C^{[1]}(\vec{r})\right]^{[2]}\right]^{[k]}$$
$$=3\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\frac{1}{r^5}(1010|20)C^{[2]}(\vec{r})\right]^{[k]}$$
$$=3(1010|20)\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\frac{1}{r^5}C^{[2]}(\vec{r})\right]^{[k]}, \quad (27)$$

$$\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\frac{1}{r^5}C^{[2]}(\vec{r})\right]^{[k]}=\sum_i\left[\nabla^{[1]}\left[\nabla^{[1]}\frac{1}{r^5}C^{[2]}(\vec{r})\right]^{[i]}\right]^{[k]}((11)22|1(12)i)^{[k]}, \quad (28)$$

$$\left[\nabla^{[1]}\frac{1}{r^5}C^{[2]}(\vec{r})\right]^{[i]}=-5(1020|30)\frac{1}{r^7}C^{[3]}(\vec{r})\delta_{i,3}, \quad (29)$$

$$\left[[\nabla^{[1]}\nabla^{[1]}]^{[2]}\frac{1}{r^5}C^{[2]}(\vec{r})\right]^{[k]}=-5(1020|30)((11)22|1(12)3)^{[k]}\left[\nabla^{[1]}\frac{1}{r^7}C^{[3]}(\vec{r})\right]^{[k]}. \quad (30)$$

$$\left[\nabla^{[1]}\frac{1}{r^7}C^{[3]}(\vec{r})\right]^{[k]}=\left[\frac{-7C^{[1]}(\vec{r})}{r^9}C^{[3]}(\vec{r})+\frac{\sqrt{21}}{r^7}C^{[2]}(\vec{r})\right]^{[k]}$$
$$=\frac{1}{r^7}-7(-1)^{(k-4)/2}(1030/k0)C^{[k]}(\vec{r})+\sqrt{21}C^{[2]}(\vec{r}). \quad (31)$$

It is straightforward to show that only $k=4$ term survives.

$$[[\nabla^{[1]}\nabla^{[1]}]^{[2]}[\nabla^{[1]}\nabla^{[1]}]^{[2]}]^{[k]}\frac{1}{r}$$
$$=-5(1020|30)((11)22|1(12)3)^{[4]}(-7)(1030|40)C^{[4]}(\vec{r})\frac{1}{r^5}. \quad (32)$$

Here again only one type of irreducible tensor mediates the interaction between two multipoles. Only maximum rank anisotropy compatible with triangular inequality is allowed.

Let us do the same thing for one more particular term, octapole-quadrupole interaction. Then, we will show that the same thing holds for any multipole-multipole interaction.

$$[[\nabla^{[1]}\nabla^{[1]}\nabla^{[1]}]^{[3]}[\nabla^{[1]}\nabla^{[1]}]^{[2]}]^{[k]}\frac{1}{r}$$
$$=-\left[[\nabla^{[1]}\nabla^{[1]}\nabla^{[1]}]^{[3]}\left[\nabla^{[1]}\frac{C^{[1]}(\vec{r})}{r^3}\right]^{[2]}\right]^{[k]}$$
$$=3(1010|20)\left[[\nabla^{[1]}\nabla^{[1]}\nabla^{[1]}]^{[3]}\frac{1}{r^5}C^{[2]}(\vec{r})\right]^{[k]}. \quad (33)$$

If we recouple the last term, we have the following term except constant factor,

$$[[\nabla^{[1]}\nabla^{[1]}]^{[i]}\left[\frac{1}{r^5}C^{[2]}\right]^{[i']}]^{[k]}$$

$$=-5(1020|30)[[\nabla^{[1]}\nabla^{[1]}]^{[i]}\frac{1}{r^7}C^{[3]}(\hat{r})]^{[k]}\delta_{i',3}$$

$$=-5(1020|30)\sum_i[\nabla^{[1]}[\nabla^{[1]}\frac{1}{r^7}C^{[3]}(\hat{r})]^{[i]}]^{[k]}\delta_{i',3}$$

$$=-5(1020|30)\sum_i[\nabla^{[1]}[-\frac{7}{r^7}(1030|40)C^{[4]}(\hat{r})]]^{[k]}\delta_{i',3}\delta_{l,0}$$

$$=(-5)(-7)(1020|30)(1030|40)\left[\frac{1}{r^9}C^{[4]}(\hat{r})\right]^{[k]}. \tag{34}$$

As we will show in a general way, the last term is the irreducible tensorial set. Thus in this case, too, the anisotropy of the space that mediates the interaction between two multipoles is described by one irreducible tensor, the highest rank among compatible ones with triangular inequalities.

Fano-Racah's recoupling technique can be applied to general multipole-multipole interaction. First we notice that

$$M^{[k_1]}\cdot\Big[\overbrace{\nabla^{[1]}\nabla^{[1]}\cdots\nabla^{[1]}}^{k_1}\Big]^{[k_1]}M^{[k_2]}\cdot\Big[\overbrace{\nabla^{[1]}\nabla^{[1]}\cdots\nabla^{[1]}}^{k_2}\Big]^{[k_2]}$$

$$=\sum_k[M^{[k_1]}M^{[k_1]}]^{[k]}\cdot\Big[\Big[\overbrace{\nabla^{[1]}\nabla^{[1]}\cdots\nabla^{[1]}}^{k_1}\Big]^{[k_1]}\Big[\overbrace{\nabla^{[1]}\nabla^{[1]}\cdots\nabla^{[1]}}^{k_2}\Big]^{[k_2]}\Big]^{[k]}. \tag{35}$$

Keesom transformation and its generalization is based on the following chain:

$$\frac{C^{[0]}}{r}\xrightarrow{\nabla}\frac{C^{[1]}}{r^3}\xrightarrow{\nabla}\frac{C^{[2]}}{r^5}\xrightarrow{\nabla}\frac{C^{[3]}}{r^7}\xrightarrow{\nabla}\cdots \tag{36}$$

Using the above chain, the second term in the sum of Eq. (35) is reduced to the irreducible tensor. This can be proved as follows:

$$\nabla\left[\frac{C^{[k]}(\hat{r})}{r^{2k+1}}\right]$$

$$=-(2k+1)\frac{C^{[1]}(\hat{r})}{r^{2k+3}}\,C^{[k]}(\hat{r})+\frac{\sqrt{k(2k+1)}}{r^{2k+1}}\,C^{[k-1]}(\hat{r})$$

$$=-\sum_i(2k+1)(-1)^{(k+1-i)/2}(10k0|i0)\frac{C^{[i]}(\hat{r})}{r^{2k+3}}$$

$$+\frac{\sqrt{k(2k+1)}}{r^{2k+1}}\,C^{[k-1]}(\hat{r})$$

$$=-(-)^{k+1}(2k+1)(-1)\sqrt{2k-1}\begin{pmatrix}1 & k-1 & k\\ 0 & 0 & 0\end{pmatrix}\frac{C^{[k-1]}(\hat{r})}{r^{2k+1}}$$

$$-(-)^{k+1}(2k+1)\sqrt{2k+3}\begin{pmatrix}1 & k & k+1\\ 0 & 0 & 0\end{pmatrix}\frac{C^{[k+1]}(\hat{r})}{r^{2k+3}}$$

$$+\sqrt{k(2k+1)}\frac{C^{[k-1]}(\hat{r})}{r^{2k+1}}=-\sqrt{(k+1)(2k+1)}\frac{C^{[k+1]}(\hat{r})}{r^{2k+3}}. \tag{37}$$

Conclusion

In this paper, we have seen that anisotropy of the space that mediates the interaction of two multipoles should be of irreducible tensor type whose rank is the highest allowed for the system. The absense of the lower anisotropies is one of characteristics of Coulomb interaction. Keesom transformation is derived as its simplest case. It might be an interesting application to apply the techniques developed in this paper to the potentials whose forms are not given by multipole-multipole interactions.

Appendix A. On the standardization

When we use the formulas in Fano-Racah's book, we have to be careful on the standardization. Many formulas derived there are specific to the standard sets defined there. Unfortunately, their standard sets are not the one of people's choice. Condon-Shortley's one is more widely adopted. Also, either this kind of problem seems not emphasized much or not well recognized. Let us first describe the difference between Condon-Shortley and Fano-Racah convention. The formulas that depend on the standardization and thus need care when used with the usual spherical harmonics will be described later.

Both convention are same in that J_x and J_z operators are taken as real and J_y imaginary. With such choice the phases of the eigenfunctions of J_z are still at our disposal. In Condon-Shortley convention phases are determined by

$$L_+Y_{lm}=\hbar\sqrt{(l-m)(l+m+1)}Y_{l,m+1}. \tag{38}$$

Let us denote the undetermined phase of the spherical harmonics by α_m, namely

$$Y_{lm}=\alpha_m\left[\frac{(2l+1)(l-m)}{4\pi(l+m)!}\right]^{1/2}P_l^m(\cos\theta)e^{im\phi}. \tag{39}$$

If we apply $L_+=\hbar e^{i\phi}(\partial/\partial\theta+i\cot\theta(\partial/\partial\phi))$ on Y_{lm} and make use of the recurrence relation among P_l^m, then we get

$$L_+Y_{lm}=\hbar\frac{\alpha_m}{\alpha_{m+1}}\sqrt{(l-m)(l+m+1)}Y_{l,m+1}. \tag{40}$$

Condon-Shortley phase α_m thus satisfies

$$-\frac{\alpha_m}{\alpha_{m+1}}=1. \tag{41}$$

One solution may be $\alpha_m=(-1)^m$, which was the actual choice of Condon-Shortley.

Fano-Racah used $D_j(\pi)$ for the unitary matrix U that transforms the cogredient sets into contragredent ones in order to fix the phases. As Fano-Racah's book does not show explicitly why they multiply i^l to the Condon-Shortley's spherical harmonics to make them contrastandard sets, we will give the derivation of it here.

For the real set, U matrix is 1. For the linear substitution A that transforms the real set into the spherical harmonics, U changes into

$$U'=A^*UA^{-1}=A^*A^{-1}. \tag{42}$$

Now for the conventional spherical harmonics

$$Y_{1\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi},$$

$$Y_{10}=\sqrt{\frac{3}{4\pi}}\cos\theta, \tag{43}$$

the substitution A is obtained by the following relation

$$\begin{pmatrix}Y_{11}\\ Y_{10}\\ Y_{1-1}\end{pmatrix}=\begin{pmatrix}-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}i} & 0\\ 0 & 0 & 1\\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}i} & 0\end{pmatrix}\begin{pmatrix}Y_{1x}\\ Y_{1y}\\ Y_{1z}\end{pmatrix}=A\begin{pmatrix}Y_{1x}\\ Y_{1y}\\ Y_{1z}\end{pmatrix} \tag{44}$$

Then U' is obtained as

$$U'=\begin{pmatrix} -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}i} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}i} & 0 \end{pmatrix}\begin{pmatrix} -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}i} & 0 & -\frac{1}{\sqrt{2}i} \\ 0 & 1 & 0 \end{pmatrix}=\begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}. \quad (45)$$

This U' is different from $D_y(\pi)$. Now we want substitution cA so that

$$U''=(c^*)^2U'=\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}. \quad (46)$$

Two solutions i, $-i$ of c are possible. The former is the choice of the Fano-Racah's book. Thus in order to have U as the rotation matrix about y axis, the standard set of spherical harmonics should differ from the Condon-Shortly one by a multiplication constant i^l.

In Fano-Racah's book, formulas that contain U matrix are subject to the choice of the sets. For example, the following formula

$$\sqrt{2j+1}[a^{(j)}b^{(j)}]^{(0)}=a^{(j)}\cdot b^{(j)}, \quad (47)$$

should be modified for the Condon-shortley sets as

$$(-1)^j\sqrt{2j+1}[a^{(j)}b^{(j)}]^{(0)}=a^{(j)}\cdot b^{(j)}. \quad (48)$$

The reason for the change is that the right hand side of the above equationis invariant under substitution while the left hand side of the equation suffers from change under the substitution $c(=i^j)$. Let the set $a^{(j)}$ be related to the Condon-Shortley set $\alpha^{(j)}$ by $a^{(j)}=c\alpha^{(j)}$. Then $[a^{(j)}b^{(j)}]^{(0)}$ becomes $c^2[\alpha^{(j)}\beta^{(j)}]^{(0)}$. On the other hand, $a^{(j)}\cdot b^{(j)}$ should be invariant under substitution by definition. Another nontrivial example occurs when we try to relate $[a^{(j)}b^{(j)}]^{(1)}$ to the vector product. Here, the source of the problem is the same as above. The vector product is invariant under any substitution while $[a^{(j)}b^{(j)}]^{(1)}$ is not. Thus we encounter the imaginary number in such a connection when the Condon-Shortley sets are used: $[\alpha^{(1)}\beta^{(1)}]^{(1)}=-i/\sqrt{2}(\mathbf{x}\times\mathbf{y})$. If Fano-Racah's standard sets are used, the imaginary number does not appear.

Appendix B. On the multipole expansion

Let us consider the electrostatic potential energy between two charge distributions ρ_1 and ρ_2. Here it is assumed that two charge distributions are far apart. The electrostatic potential is given by

$$V=\int\frac{\rho_1(\vec{x}_1)\rho_2(\vec{x}_2)}{|\vec{x}_2-\vec{x}_1|}\,d\vec{x}_1d\vec{x}_2, \quad (49)$$

$\vec{x}_1$ and $\vec{x}_2$ are vectors measured from the origin O. Let us consider the vectors $\vec{r}_1$ and $\vec{r}_2$ measured from the centers of each fragment. If $\vec{r}_{10}$ and $\vec{r}_{20}$ are the vectors of the centers of fragments measured from the origin O, then $\vec{x}_1=\vec{r}_1+\vec{r}_{10}$ and $\vec{x}_2=\vec{r}_2+\vec{r}_{20}$. Since two charge distributions are far apart, we can make a Taylor expansion:

$$\frac{1}{x}=\frac{1}{|\vec{r}_2-\vec{r}_1+\vec{r}|}=\frac{1}{r}+\vec{r}_1\cdot\nabla_1\frac{1}{|\vec{r}_2-\vec{r}_1+\vec{r}|}\Big|_{r_1'=r_2'=0}\vec{r}_2\cdot\nabla_2\frac{1}{|\vec{r}_2-\vec{r}_1+\vec{r}|}\Big|_{r_1'=r_2'=0}+\cdots=\frac{1}{r}+\vec{r}_1\cdot\nabla\frac{1}{r}\ \vec{r}_2\cdot\nabla\frac{1}{r}+\cdots. \quad (50)$$

Then the electrostatic potential may be rewritten as

$$V=\frac{q_1q_2}{r}+q_1(\vec{\mu}_2\cdot\nabla_2)\frac{1}{r}+q_2(\vec{\mu}_1\cdot\nabla_1)\frac{1}{r}+(\vec{\mu}_1\cdot\nabla_1)(\vec{\mu}_2\cdot\nabla_2)\frac{1}{r}\cdots+\left[\int(-1)^{k_1}(\vec{r}_1\cdot\nabla)^{k_1}(\vec{r}_2\cdot\nabla)^{k_2}\rho_1(\vec{r}_1)\rho_2(\vec{r}_2)d\vec{r}_1d\vec{r}_2\right]\frac{1}{r}+\cdots. \quad (51)$$

The general term has a rather inconvenient form. The preferrable form maybe the following

$$\mathrm{M}^{(k_1)}\cdot[\nabla\nabla\cdots\nabla]^{(k_1)}M^{(k_2)}\cdot[\nabla\nabla\cdots\nabla]^{(k_2)}. \quad (52)$$

Let us show that this is the case for $k_1=2$ and $k_2=1$:

$$V_{2-1}\equiv\left[\int(\vec{r}_1\cdot\nabla)(\vec{r}_1\cdot\nabla)\rho(\vec{r}_1)d\vec{r}_1\int(\vec{r}_2\cdot\nabla)\rho(\vec{r}_2)d\vec{r}_2\right]\frac{1}{r}. \quad (53)$$

We now want to apply Fano-Racah's recoupling theory. According to this theory, we first rewrite the scalar products of two vectors to the zeroth-rank irreducible tensors of direct products of two spherical tensors. Namely, $\vec{r}_1\cdot\nabla=\sqrt{3}[r_1^{[1]}\nabla^{[1]}]^{[0]}$. Beware that this relation depends on the convention of the sets. In particular, it only holds for the sets of Fano-Racah convention. On this understanding, let us first simplify the integrand of the first integral of V_{2-1}.

$$(\vec{r}_1\cdot\nabla)(\vec{r}_1\cdot\nabla)=\sum_k[r_1^{[1]}r_1^{[1]}]^{(k)}\cdot[\nabla^{[1]}\nabla^{[1]}]^{(k)}. \quad (54)$$

As $r_1^{[1]}$ equals $C_1^{[1]}$

$$[r_1^{[1]}r_1^{[1]}]^{(k)}=[C_1^{[1]}C_1^{[1]}]^{(k)}=i^{1+1-k}(1010|k0)C_1^{(k)}=-\frac{1}{\sqrt{3}}\delta_{k0}+\frac{\sqrt{6}}{3}C_1^{[1]}\delta_{k2}. \quad (55)$$

Then by using the fact that $[\nabla^{[1]}\nabla^{[1]}]^{(0)}\frac{1}{r}=0$

$$\int(\vec{r}_1\cdot\nabla)(\vec{r}_1\cdot\nabla)\rho(\vec{r}_1)d\vec{r}_1=\frac{\sqrt{6}}{3}\left[\int C_1^{[2]}\rho(\vec{r}_1)d\vec{r}_1\right]\cdot[\nabla^{[1]}\nabla^{[1]}]^{(2)}\frac{1}{r}=\frac{\sqrt{6}}{3}Q_2^{[1]}\cdot[\nabla^{[1]}\nabla^{[1]}]^{(2)}\frac{1}{r}, \quad (56)$$

where the quadrupole moment is defined as $Q_1^{[2]}=\int C_1^{[2]}\rho(\vec{r}_1)d\vec{r}_1$. As a whole,

$$V_{2-1}=(Q_1^{[2]}\cdot[\nabla^{[1]}\nabla^{[1]}]^{(2)})\cdot(\vec{\mu}_2\nabla)\frac{1}{r}. \quad (57)$$

Appendix C. Action of gradient operator on solid harmonics

The result of the application of a gradient operator on a solid harminic can be obtained in analytic forms by making use of the following definition of the solid harmonic:

$$\frac{(\vec{a}\cdot\vec{r})^{(k)}}{2^kk!}=\sum_q\phi_{kq}(\vec{a})C^{[k]}, \quad (58)$$

where $\vec{a}$ is the vector of length zero defined as

$$\vec{a}=(-z_+{}^2+z_-{}^2,\ -i(z_+{}^2+z_-{}^2),\ 2z_+z_-), \tag{59}$$

and $\phi_{kq}(z)$ is defined as

$$\phi_{kq}(z)=\frac{z_+{}^{k+q}z_-{}^{k-q}}{\sqrt{(k+q)!(k-q)!}}. \tag{60}$$

If we differentiate both sides of Eq. (58), we obtain

$$\frac{\vec{a}}{2}\,\frac{(\vec{a}\cdot\vec{r})^{(k-1)}}{2^{k-1}(k-1)!}=\sum_q \phi_{kq}(z)\nabla C^{[k]}. \tag{61}$$

If we make the coefficients of $\phi_{kq}(z)$ of Eq. (61) zero, the following relations are obtained:

$$\nabla_1{}^{[1]}C_q{}^{[k]}=\sqrt{\frac{(k-q)(k-q-1)}{2}}\ C_{q+1}^{[k-1]},$$

$$\nabla_0{}^{[1]}\nabla_q{}^{[k]}=-\sqrt{(k^2-q^2)}C_{q+1}{}^{[k-1]},$$

$$\nabla_{-1}^{[1]}C_q{}^{[k]}=\sqrt{\frac{(k+q)(k+q-1)}{2}}\ C_{q-1}^{[k-1]}. \tag{62}$$

On the other hand, by the well known vector coupling theory, $\nabla_{q'}{}^{[1]}C_q{}^{[k]}$ can be decomposed into irreducible products $[\nabla^{[1]}C^{[k]}]_{q+q'}{}^{[K]}$ with the expansion coefficients given by the Wigner coefficients as follows:

$$\begin{aligned}\nabla_{q'}{}^{[1]}C_q{}^{[k]}&=\textstyle\sum_K(1q'kq|Kq+q')[\nabla^{[1]}C^{[k]}]_{q+q'}^{(K)}\\ &=(1q'kq|k-1q+q')[\nabla^{[1]}C^{[k]}]_{q+q'}^{[k-1]}.\end{aligned} \tag{63}$$

From Eqs. (62) and (63), we obtain Eq. (21).

References

1. Howard, M. J.; Smith, I. W. M. *Prog. React. Kinet.* **1983**, *12*, 55.
2. (a) Quack, M.; Tröe, J. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 240. (b) Quack, M.; Tröe, J. *ibid*, **1983**, *81*, 329. (c) Tröe, J. *J. Chem. Phys.* **1983**, *79*, 6017.
3. (a) Wardlaw, D. M.; Marcus, R. A. *J. Chem. Phys.* **1985**, *83*, 3462. (b) Wardlaw, D. M.; Marcus, R. A. *J. Phys. Chem.* **1986**, *90*, 5383.
4. Klippenstein, S. J.; Marcus, R. A. *J. Chem. Phys.* **1988**, *92*, 3105.
5. Lee, C. W. *Research Review of Science and Engineering* **1995**, *12*, 221; Ajou University: Suwon, Korea.
6. Clary, D. C. *Mol. Phys.* **1984**, *53*, 3.
7. Keesom, W. H. *Communications from the Physical Laboratory of the University of Leiden*, Supplement No. 24b, p 121-132.
8. Fano, U.; Racah, G. *Irreducible tensorial sets*; Academic: New York, 1959.
9. Edmonds, E. R. *Angular momentum in Quantum Mechanics*; Pricenton: Princeton, 1957.
10. Condon, E. U.; Shortley, G. H. *The Theory of Atomic Spectra*; Cambridge, Cambridge University press, 1935.

Application of Multichannel Quantum Defect Theory to the Triatomic van der Waals Predissociation Process II

Chun-Woo Lee

Department of Chemistry, Ajou University, 5 Wonchun Dong, Suwon 441-749, Korea

Received June 29, 1995

Generalized Multichannel Quantum Defect theory (MQDT) was implemented to the vibrational predissociation of triatomic van der Waals molecules in the previous paper [*Bull. Korean Chem. Soc*, **12**, 228 (1991)]. Implementation was limited to the calculation of the scattering matrix. It is now extended to the calculation of the predissociation spectra and the final rotational distribution of the photofragment. The comparison of the results with those obtained by other methods, such as Golden-rule type calculation, infinite order sudden approximation (IOS), and close-coupling method, shows that the implementation is successful despite the fact that transition dipole moments show more energy dependence than other quantum defect parameters. Examination of the short-range channel basis functions shows that they resemble angle-like functions and provide the validity of the IOS approximation. Besides the validity of the latter, only a few angles are found to play the major role in photodissociation. In addition to the implementation of MQDT, more progress in MQDT itself is made and reported here.

Introduction

Photodissociation provides a wealth of information on molecular dissociation dynamics, as it may be visualized as a half collision process. Traditionally the total dissociation cross sections as functions of the photon energies were measured. However, in an increasing number of recent experiments, final state distributions of the photofragments have been measured. Such experiments were made possible by the availability of powerful light sources and by the development of efficient detection methods like laser induced fluorescence or resonance enhanced multiphoton ionization, and so on. Reliable intermolecular potentials have been deduced from such sophisticated experimental data. Details of photo-